



Chapter E

Determination of Total Alkalinity using a preset endpoint (pH 4.5) Autotitration System

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Principle

Alkalinity is defined as the capacity of water to neutralize a strong acid to a designated pH, usually 4.5. It is the sum of all the titratable bases, and it is determined by titration with a standardized solution of a strong mineral acid.

In the classical colorimetric determination of alkalinity by titration with acid, Phenolphthaline is used to indicate the pH 8.3 endpoint, and Methyl Orange to indicate the pH 4.5 endpoint. Alkalinity determined with reference to these two endpoints is often called “P and M alkalinity”. The terminology is still in use, even though it is more usual today to use a calibrated pH electrode as an endpoint indicator. The “total alkalinity” is based on the amount of acid required to neutralize the sample to the pH 4.5 endpoint; in many determinations of alkalinity, especially in natural waters where there is no hydroxide present, the only result required is “total alkalinity”. Both types of alkalinity are usually expressed in units of ppm (or mg/L) calcium carbonate. To measure “total alkalinity”, a preset endpoint of pH 4.5 is used for the titration.

Interferences

Alkalinity can be stable in water samples for extended periods of time, but in waters that are not in equilibrium, such as mine-drainage waters, irreversible changes may take place during storage. Therefore, alkalinity should be determined as soon as possible after sample collection. Because of time constraints in the field, we often refrigerate the water samples and measure alkalinity immediately on returning to the laboratory. If there is any question about the stability of alkalinity, the analysis should be done at the sample site.

If the ORION 960 detects a problem during analysis, an assistance message will be displayed and printed. The analysis usually will not be automatically stopped.

If samples are left uncapped for prolonged periods, highly alkaline solutions will absorb CO₂ from the air resulting in positive biases.

Scope

If the only anions present in a solution, with pH >8.3, are hydroxide and carbonate there will be two endpoints in the titration with acid. The first endpoint occurs at about pH 8.3 and corresponds to the hydroxide and half the carbonate,

the second endpoint occurs at about pH 4.5 and corresponds to the rest of the carbonate. Waters with pH between 4.5 and about 8.3 will most likely have only bicarbonate alkalinity.

This method is applicable to the analysis of natural waters and leachate solutions. It can run 80 samples per day with an alkalinity between 3ppm and 500 ppm. Above 500 ppm the samples will have to be diluted and rerun.

Apparatus

- Orion 960 Autochemistry System
- Orion 940 pH/ISE Meter; The heart of Orion 960 Autochemistry System
- Orion 960 Module; contains the electronics, AUTODispenser, software, and electrode tower and forms the base for the complete system
- Printer
- Orion 960SC Sample Changer
- Electrode Tower Attachment
- 15 (125mL) plastic beakers
- Stirrer
- Automatic Temperature Compensator (ATC) Probe
- pH Electrode

Reagents

- Deionized water (DI)
- Titrant 0.01M H₂SO₄. (Prepared by diluting 100mL of 0.05M H₂SO₄ with 400mL deionized water)

Safety Precautions

Normal laboratory safety procedures should be followed. Protective clothing, gloves, safety glasses, and fume hood should be used when handling sulfuric acid. The operator should take care when analyzing samples of an unknown nature. Refer to the CHP and MSDS for specific precautions, effects of overexposures, and first-aid treatment for the reagent used in this method.

Procedure

Prior to starting the analyses, accessories and method parameter such as, the technique to be used, volume of sample, concentration of titrant, predose amount to be added if any, pH of endpoint, rinse time, stirring time, number of samples and sample ID are recorded in the method or sequence to be used in the Orion 960 Autochemistry System. Once these operating parameters have been input and the pH electrode calibrated for the expected sample range analysis may begin.

- Measure 50 mL of sample into a 150 mL beaker for the desired number of samples to be analyzed.

- Place the samples in the sample changer
- Once the “ Begin Analysis “ command has been given, the Orion 960 Autochemistry System controls all operations and monitors the working cycle.
- The method used and the results of analysis are printed after each sample has been analyzed.
- Upon completion of the analysis, the sample beakers are removed from the sample changer and poured into the satellite accumulation storage container to be neutralized for disposal in accordance with the established waste disposal protocol

Assignment of Uncertainty

Table 1.-Analytical performance summary for alkalinity (ppm CaCO₃) by the Preset Endpoint Method

Reference materials are water samples with pv from Water Resources Division,(USGS OPF 96-436, 97-20, 96-138, 97-553).

<i>Reference</i>	<i>Description</i>	<i>n</i>	<i>Mean</i>	<i>s</i>	<i>pv</i>	<i>% RSD</i>	<i>% R</i>
M-138	major constituents	10	38.847	3.142	41.10	8.087	106
M-130	major constituents	20	56.936	1.910	60.0	3.354	105
M-140	major constituents	13	112.94	1.178	114.0	1.043	101
M-136	major constituents	27	152.20	2.266	152.0	1.489	99.9
M-142	major constituents	10	181.60	3.959	180.0	2.180	99.1

See page ix of the introduction to this Methods Manual for an explanation of the abbreviations used in the analytical performance summary tables.

Bibliography

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